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(71)Applicant : SAMSUNG ELECTRON CO LTD

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(72)Inventor : KYO SHOHAN  
PARK CHANG-SOO  
SAI INSHUKU  
LEE SANG-IN

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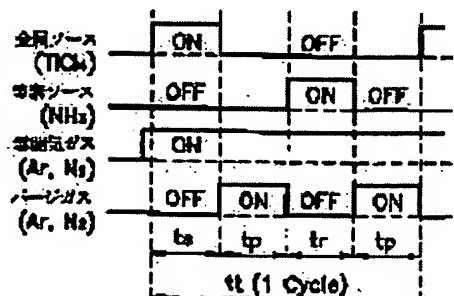
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(54) FORMATION OF METALLIC NITRIDED FILM BY CHEMICAL VAPOR PHASE DEPOSITION AND FORMATION OF METALLIC CONTACT OF SEMICONDUCTOR DEVICE USING THIS FORMATION

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a method for forming a metallic nitrided film by a chemical vapor phase deposition method and to provide a method for forming a metallic contact of a semiconductor device using.

SOLUTION: This method has a stage in which a semiconductor substrate is charged into a vapor depositing chamber, a stage in which a metallic source is flowed into the vapor depositing chamber, a stage in which a purge gas is flowed into the vapor depositing chamber, and the metallic source remaining in the vapor depositing chamber is removed, a stage in which the inflow of the purge gas is cut off, the nitrogen source gas is flowed into the vapor depositing chamber so as to be reacted with the metallic source adsorbed by the semiconductor substrate and a stage in which the inflow of the nitrogen source gas is cut off, the purge gas is flowed into the vapor depositing chamber and the nitrogen source remaining in the vapor depositing chamber is removed, and a metallic nitrided film is formed on the semiconductor substrate. In this way, the



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metallic nitrided film having low specific resistance and a low Cl content while being excellent in level difference applicability at a low temp. of  $\leq 500^{\circ}\text{C}$  can be obtd., whose deposition rate is about 20  $\text{\AA}/\text{cycle}$ , and it is also suitable for mass production.

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**CLAIMS**


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[Claim(s)]

[Claim 1] In the metal nitride formation approach by the chemistry gaseous-phase vacuum deposition which uses the metal source and the nitrogen source as a precursor (a) The phase which inserts a semiconductor substrate in the vacuum evaporator interior of a room, and the phase of pouring the (b) aforementioned metal source to the vacuum evaporator interior of a room, (c) The phase of removing said metal source which intercepts the inflow of said metal source, passes purge gas to the vacuum evaporator interior of a room, and remains to the vacuum evaporator interior of a room, (d) Said metal source which intercepted the inflow of said purge gas, poured the nitrogen source to the vacuum evaporator interior of a room, and adsorbed on said semi-conductor substrate, and the phase of making it reacting, (e) The metal nitride formation approach characterized by providing the phase of removing said nitrogen source which intercepts the inflow of said nitrogen source, passes purge gas to the vacuum evaporator interior of a room, and remains to the vacuum evaporator interior of a room, and forming a metal nitride on said semi-conductor substrate.

[Claim 2] Said metal source  $\text{TiCl}_4$ ,  $\text{TiCl}_3$ ,  $\text{TiI}_4$ , and  $\text{TiBr}_2$ ,  $\text{TiF}_4$ , 2 (C five H5)  $\text{TiCl}_2$ , and 2 (5 (CH3) C5)  $\text{TiCl}_2$ , C5 H5  $\text{TiCl}_3$ , C9 H10BCl3 N6 Ti, and C9 H7  $\text{TiCl}_3$ , (C5 5 (CH3))  $\text{TiCl}_3$  and  $\text{TiCl}_4$  2 (NH3) And (CH3) 5 C5 Ti3 (CH3) It is at least one chosen from the becoming group. Said nitrogen source is NH3. The metal nitride formation approach according to claim 1 characterized by carrying out and forming a titanium nitride.

[Claim 3] Vacuum evaporator temperature is the metal nitride formation approach according to claim 2 characterized by being 400-500 degrees C.

[Claim 4] The pressure of said vacuum evaporator interior of a room is the metal nitride formation approach according to claim 2 characterized by being 1 - 20torr.

[Claim 5] Said metal source is TDEAT or TDMAT, and said nitrogen source is NH3. The metal nitride formation approach according to claim 1 characterized by carrying out and forming a titanium nitride.

[Claim 6] It is the metal nitride formation approach according to claim 5 which vacuum evaporator temperature is 250-400 degrees C, and is characterized by the pressure of said vacuum evaporator interior of a room being 0.1 - 10torr.

[Claim 7] Said metal source is  $\text{TaBr}_5$ ,  $\text{TaCl}_5$ ,  $\text{TaF}_5$ , and  $\text{TaI}_5$ . And (C5 5 (CH3))  $\text{TaCl}_4$  It is at least one chosen from the becoming group, and said nitrogen source is NH3. The metal nitride formation approach according to claim 1 characterized by carrying out and forming a tantalum nitride.

[Claim 8] Vacuum evaporator temperature is the metal nitride formation approach according to claim 7 characterized by being 400-500 degrees C.

[Claim 9] The pressure of said vacuum evaporator interior of a room is the metal nitride formation approach according to claim 7 characterized by being 1 - 20torr.

[Claim 10] said purge gas -- Ar or N2 it is -- the metal nitride formation approach according to claim 1 characterized by things.

[Claim 11] Said metal source which flows into said vacuum evaporator interior of a room is the metal nitride formation approach according to claim 1 characterized by pouring a sink and said nitrogen source

by the flow rate of 5 - 200sccm for 1 - 10 seconds, and pouring a sink and said purge gas for 1 - 10 seconds by the flow rate of 10 - 200sccm for 1 - 10 seconds with the flow rate of 1 - 5sccm.

[Claim 12] The metal nitride formation approach according to claim 1 characterized by continuing and passing the controlled atmosphere between the - (e) phases (aforementioned [ a ]) to said vacuum evaporatio interior of a room in order to maintain uniformly the pressure of said vacuum evaporatio interior of a room.

[Claim 13] Said controlled atmosphere is Ar, helium, and N<sub>2</sub>. The metal nitride formation approach according to claim 12 characterized by being at least one chosen from the becoming group.

[Claim 14] The metal nitride formation approach according to claim 1 characterized by mixing conveyance gas in said metal source or the nitrogen source, and passing to said vacuum evaporatio interior of a room in order to make it said metal source or the nitrogen source flow smoothly to said vacuum evaporatio interior of a room.

[Claim 15] said conveyance gas -- Ar or N<sub>2</sub> it is -- the metal nitride formation approach according to claim 1 characterized by things.

[Claim 16] The metal nitride formation approach according to claim 1 characterized by repeating the - (e) phase (aforementioned [ b ]) and adjusting the thickness of the metal nitride vapor-deposited on said semi-conductor substrate.

[Claim 17] (a) The phase which forms the 1st metal layer on a semi-conductor substrate, and the phase which carries out the laminating of the interlayer insulation film on the 1st metal layer of (b) above, (c) The phase which etches an interlayer insulation film and forms a contact hole so that said 1st metal layer may be exposed, (d) The phase of pouring the metal source to the vacuum evaporatio interior of a room, and making the metal source sticking to an object as a result of the aforementioned (c) phase, (e) The phase of removing said metal source which intercepts the inflow of said metal source, passes purge gas, and remains to the vacuum evaporatio interior of a room, (f) Intercept the inflow of said purge gas and it is made to react with said metal source with which the nitrogen source was poured to the vacuum evaporatio interior of a room, and was adsorbed by the lifter as a result of the aforementioned (d) phase. The phase which forms the metal nitride of a barrier-metal layer on said exposed 1st metal layer and a contact hole, (g) The phase of removing said nitrogen source which intercepts the inflow of said nitrogen source, passes purge gas to the vacuum evaporatio interior of a room, and remains to the vacuum evaporatio interior of a room, (h) The metal contact formation approach of the semiconductor device characterized by including the phase which forms a metal plug in a lifter as a result of the aforementioned (g) phase, and the phase which forms the 2nd metal layer in a lifter as a result of the (i) aforementioned (h) phase.

[Claim 18] Said metal source TiCl<sub>4</sub>, TiCl<sub>3</sub>, TiI<sub>4</sub>, and TiBr<sub>2</sub>, TiF<sub>4</sub>, 2 (C five H<sub>5</sub>) TiCl<sub>2</sub>, and 2 (5 (CH<sub>3</sub>) C<sub>5</sub>) TiCl<sub>2</sub>, C<sub>5</sub> H<sub>5</sub> TiCl<sub>3</sub>, C<sub>9</sub> H<sub>10</sub>BCl<sub>3</sub> N<sub>6</sub> Ti, and C nine H<sub>7</sub> -- TiCl<sub>3</sub> and TiCl (C<sub>5</sub> 5 (CH<sub>3</sub>))<sub>3</sub> -- TiCl<sub>4</sub> 2 (NH<sub>3</sub>) And (CH<sub>3</sub>)<sub>5</sub> C<sub>5</sub> Ti<sub>3</sub> (CH<sub>3</sub>) It is at least one chosen from the becoming group. Said nitrogen source is NH<sub>3</sub>. The metal contact formation approach of the semiconductor device according to claim 17 characterized by carrying out and forming a titanium nitride as said barrier-metal layer.

[Claim 19] It is the metal contact formation approach of the semiconductor device according to claim 18 characterized by for the vacuum evaporatio temperature of the - (g) phase (aforementioned [ d ]) being 400-500 degrees C, and the pressure of the vacuum evaporatio interior of a room being 1 - 20torr.

[Claim 20] Said metal source is TDEAT or TDMAT, and said nitrogen source is NH<sub>3</sub>. The metal contact formation approach of the semiconductor device according to claim 17 characterized by carrying out and forming a titanium nitride as said barrier-metal layer.

[Claim 21] It is the metal contact formation approach of the semiconductor device according to claim 20 characterized by for the vacuum evaporatio temperature of the - (g) phase (aforementioned [ d ]) being 250-400 degrees C, and the pressure of said vacuum evaporatio interior of a room being 0.1 - 10torr.

[Claim 22] Said metal source is TaBr<sub>5</sub>, TaCl<sub>5</sub>, TaF<sub>5</sub>, and TaI<sub>5</sub>. And (C<sub>5</sub> 5 (CH<sub>3</sub>)) TaCl<sub>4</sub> It is at least one chosen from the becoming group, and said nitrogen source is NH<sub>3</sub>. The metal contact formation

approach of the semiconductor device according to claim 17 characterized by carrying out and forming a tantalum nitride as said barrier-metal layer.

[Claim 23] It is the metal contact formation approach of the semiconductor device according to claim 22 characterized by for the vacuum evaporatio no temperature of the - (g) phase (aforementioned [ d ]) being 400-500 degrees C, and the pressure of said vacuum evaporatio no interior of a room being 1 - 20torr.

[Claim 24] said purge gas -- Ar or N2 it is -- the metal contact formation approach of the semiconductor device according to claim 17 characterized by things.

[Claim 25] Said metal source which flows into said vacuum evaporatio no interior of a room is the metal contact formation approach of the semiconductor device according to claim 17 characterized by pouring a sink and said nitrogen source by the flow rate of 5 - 200sccm for 1 - 10 seconds, and pouring a sink and said purge gas for 1 - 10 seconds by the flow rate of 10 - 200sccm for 1 - 10 seconds with the flow rate of 1 - 5sccm.

[Claim 26] In order to maintain uniformly the pressure of said vacuum evaporatio no interior of a room between the - (g) phases (aforementioned [ d ]), it is Ar, helium, and N2. The metal contact formation approach of the semiconductor device according to claim 17 characterized by continuing and passing at least one controlled atmosphere chosen from the becoming group to said vacuum evaporatio no interior of a room.

[Claim 27] The metal contact formation approach of the semiconductor device according to claim 17 characterized by repeating the - (g) phase (aforementioned [ d ]) and adjusting the thickness of the barrier-metal layer vapor-deposited on said 1st metal layer and a contact hole.

[Claim 28] Said 1st metal layer is the metal contact formation approach of the semiconductor device according to claim 17 characterized by being aluminum.

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## DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the manufacture approach of a semiconductor device, and relates to the metal nitride formation approach by the chemistry gaseous-phase vacuum deposition (it considers as Chemical Vapor Deposition and Following CVD) which uses the metal source and the nitrogen source for a detail as a precursor, and the metal contact formation approach of the semiconductor device using this.

[0002]

[Description of the Prior Art] For stabilization of the contact interface of a semiconductor device, the barrier-metal layer which carries out the role which controls the counter diffusion and the chemical reaction between other matter is indispensable. Although a metal nitride like TiN, TaN, and WN is generally widely used as a barrier-metal layer of such a semiconductor device, TiN is the typical matter also in this.

[0003] However, when manufacturing a metal nitride like TiN by the sputtering approach, there is a problem in applying to the semiconductor device which level difference spreading nature is low and integrates highly in order. The cross section at the time of forming the beer contact for connection during metal wiring (via contact) as an example is shown in drawing 9 A and drawing 9 B. Drawing 9 A and drawing 9 B show simple beer contact and support beer contact respectively, and are as follows like the formation fault. After forming the 1st metal layer 30 which consists of aluminum on the semiconductor substrate 20 and forming the TiN film 40 by the sputtering approach as capping film on it, the laminating of the interlayer insulation films 50 and 51 is carried out. subsequently -- the -- one -- a metal -- a layer -- 30 -- a top -- an interlayer insulation film -- etching -- a contact hole -- forming (the process which forms Support A by wet chemical engraving being added in drawing 9 B) -- a glue line -- Ti -- and -- a barrier metal -- a layer -- TiN -- the film -- 60 -- 61 -- having vapor-deposited -- after -- a CVD method -- a contact hole -- filling -- a tungsten -- (-- W --) -- a plug -- 70 -- 71 -- forming. Henceforth, chemical machinery-polish and etchback remove the tungsten for the upper part, and connection between metal wiring is completed by carrying out the laminating of the 2nd metal layer on it (this process was not shown).

[0004] Here, although the conventional approach vapor-deposits the TiN film 60 and 61 of a barrier-metal layer by the sputtering approach which is not good, by the part A which forms the base of a contact hole, dark circles, and support, the thickness of the TiN film becomes thin as the aspect ratio of beer becomes large. Therefore, WF6 Ti or whose aluminum is tungsten source gas by the part where the thickness is thin at the time of tungsten vacuum evaporatio~~no~~ of a consecutiveness process TiFX which it combines with a residual fluorine and is an insulator layer Or AlFX It forms and the poor contact X is invited.

[0005] When increasing vacuum evaporatio~~no~~ time amount and making the thickness of the TiN film 60 and 61 increase as an approach of removing such poor contact, after the thickness of the TiN film increasing, and the upper part of a contact hole becoming narrow or closing only the upper part of a

contact hole, possibility that a void will occur at the time of tungsten vacuum evaporation is high. Therefore, in order to apply TiN to contact with a large aspect ratio, the process at which the level difference spreading property has been improved is needed. Therefore, the production process of the metal nitride (henceforth a CVD-metal nitride) by the CVD method has been studied as a next-generation process.

[0006] The metal source 4 which generally contains chlorine (Cl) at a CVD-metal nitride process (source of a metal), for example, TiCl<sub>4</sub>. A precursor [ like ] is used. TiCl<sub>4</sub>. Although the CVD-metal nitride used as a precursor has 95% or more of high level difference spreading nature and has the advantage in which an evaporation rate is quick, there is a problem in which Cl remains as an impurity within a metal nitride. Thus, Cl which remains in a metal nitride as an impurity makes specific resistance high for the corrosion problem of metal wiring like aluminum with a lifting. Therefore, although it is required that Cl content which remains in a metal nitride should be reduced, and specific resistance should be made low, for that, it should vapor-deposit at high temperature. Namely, TiCl<sub>4</sub>. In order to obtain the specific resistance below 200micro ohm-cm at the CVD-metal nitride process using the metal source [ like ], the vacuum evaporation temperature of 675 degrees C of minimum is needed. However, since the vacuum evaporation temperature of 480 degrees C or less is required when vapor-depositing a metal nitride in the beer contact with which there is a problem exceeding the thermal burden limitation that the substrate film can bear, and a thermal stress limitation, and especially Si contact and aluminum are used as the substrate film, the high vacuum evaporation temperature of 600 degrees C or more cannot adopt a hot CVD-metal nitride process.

[0007] It is TiCl<sub>4</sub> as a low-temperature-evaporation CVD-metal nitride process. Although the approach of adding MH (methylhydrazine and HNNH(CH<sub>3</sub>)<sub>2</sub>) is in the metal source [ like ], there is demerit from which a level difference spreading property falls to 70% or less in this case.

[0008] As other approaches in which low temperature evaporation is possible, there is the MOCVD-metal nitride formation approach which uses the organic metal precursor of TDEAT (tetrakis diethylamino Ti and Ti<sub>4</sub> (N(CH<sub>2</sub> CH<sub>3</sub>)<sub>2</sub>)) and TDMAT (tetrakis dimethylamino Ti and Ti<sub>4</sub> (N(CH<sub>3</sub>)<sub>2</sub>)). The trouble by Cl does not occur and a MOCVD-metal nitride has the advantage in which low temperature evaporation is possible. However, carbon recognizes abundant existence of the MOCVD-metal nitride as an impurity, it shows high specific resistance, and the demerit which is not good at about 70% is in the film.

[0009] On the other hand, as other approaches which are not vacuum evaporation in order to conquer the trouble by Cl, the formation approach of the metal nitride by the atomic layer grown method (it is called atomic layer epitaxy and Following ALE) is tried. However, in order to grow up ALE per atomic layer only using chemical adsorption, there is demerit in which an evaporation rate (0.25A/cycle following) is too much slow in applying to the production process of the semiconductor device as which mass production method is required.

[0010]

[Problem(s) to be Solved by the Invention] The purpose is in this invention taking the above demerits into consideration, being thought out, and offering the approach of forming the metal nitride which is satisfied with low temperature of the level difference spreading property of having excelled though the evaporation rate was quick, low high impurity concentration, and low resistivity.

[0011] Other purposes of this invention are to apply the above-mentioned metal nitride formation approach to metal contact of a semiconductor device, and offer the metal contact formation approach of having the barrier-metal layer which is satisfied with low temperature of the level difference spreading property of having excelled though the evaporation rate was quick, low high impurity concentration, and low resistivity.

[0012]

[Means for Solving the Problem] The metal nitride formation approach of this invention for attaining the above-mentioned purpose is the metal nitride formation approach by the chemistry gaseous-phase vacuum deposition which uses the metal source (source of a metal), and the nitrogen source (nitrogen source) as a precursor, and is characterized by being made as follows. First, a semi-conductor substrate

is inserted in the vacuum evaporatio interior of a room, and the metal source is poured to the vacuum evaporatio interior of a room. The inflow of the metal source is intercepted after predetermined time, and the metal source which flows purge gas into the vacuum evaporatio interior of a room, and remains to the vacuum evaporatio interior of a room is removed. The inflow of purge gas is intercepted after predetermined time, and it is made to react with the metal source which pours the nitrogen source to the vacuum evaporatio interior of a room and by which it was adsorbed on said semi-conductor substrate. Again, the inflow of the nitrogen source is intercepted, purge gas is passed to the vacuum evaporatio interior of a room after predetermined time, the nitrogen source which remains to the vacuum evaporatio interior of a room is removed, and a metal nitride is formed on a semi-conductor substrate.

[0013] The metal nitride formation approach of this invention can repeat the gas inflow cycle passed in order of the above-mentioned metal source -> purge gas -> nitrogen source -> purge gas until it obtains the metal nitride of the thickness of a wish.

[0014] The metal source here  $TiCl_4$  (titanium chloride),  $TiCl_3$  (titanium chloride) and  $TiI_4$  (titanium iodide),  $TiBr_2$  (titanium bromide) and  $TiF_4$  (titanium fluoride), 2  $TiCl_2$  (bis(cyclopentadienyl) titanium dichloride), (C five H5) 2  $TiCl_2$  (bis(pentamethylcyclopentadienyl) titanium dichloride),  $(CH_3)_5 C_5 TiCl_3$  (cyclopentadienyltitanium trichloride),  $C_9 H_{10} BCl_3 N_6 Ti$  (hydr-otris(1-pyrazolylborato) trichloro titanium),  $C_9 H_7 TiCl_3$  (indenyltitanium trichloride),  $TiCl_3$  (pentamethylcyclopentadienyltitanium trichloride),  $(C_5 H_5)_2 TiCl_4$  2  $(NH_3)$  (tetrachlorodiaminotitanium),  $5 C_5 H_5 Ti (CH_3)_3$  (trimethylpentamethylcyclopentadienyltitanium),  $(CH_3)_3 Ti$  It is TDEAT or TDMAT and the nitrogen source can form a titanium nitride by the metal nitride as  $NH_3$ . The metal source  $TaBr_5$  (tantalum bromide) and  $TaCl_5$  (tantalum chloride),  $TaF_5$  (tantalum fluoride), It is referred to as  $TaI_5$  or (tantalum iodide)  $(C_5 H_5)_2 TaCl_4$  (pentamethylcyclopentadienyltantalum tetrachloride). It is the nitrogen source  $NH_3$  Carry out, a tantalum nitride is made to form and it gets.

[0015] Moreover, purge gas is Ar or  $N_2$ . It is desirable to use inert gas.

[0016] As for the flow rate of the metal source which flows into the vacuum evaporatio interior of a room, the nitrogen source, and purge gas, it is desirable to make it respectively like 1 - 5sccm, 5 - 200sccm, and 10 - 200sccm, and, as for the inlet time of each gas, it is desirable to make it about 1 - 10 seconds.

[0017] Moreover, in order to maintain uniformly the pressure of the vacuum evaporatio interior of a room, it is Ar, helium, or  $N_2$ . A controlled atmosphere can also be continued and passed to the vacuum evaporatio interior of a room.

[0018] It is desirable to make the vacuum evaporatio room pressure force to 0.1 - 10torr, and to make vacuum evaporatio temperature into 250-400 degrees C on the other hand, in forming the  $TiN$  film as the metal source using TDEAT or TDMAT. In using the metal source the outside of it, the vacuum evaporatio room pressure force is made to 1 - 20torr, and it makes vacuum evaporatio temperature into 400-500 degrees C.

[0019] The metal contact formation approach of this invention for attaining other above-mentioned purposes is the metal contact formation approach which forms the 1st metal layer, an interlayer insulation film, a contact hole, a barrier-metal layer, a metal plug, and the 2nd metal layer in order on a semi-conductor substrate, and the process which forms especially a barrier-metal layer is characterized by the following. That is, the metal source is poured and the metal source is made to adsorb to the semi-conductor substrate with which the contact hole which exposes the 1st metal layer to an interlayer insulation film was formed. The metal source which intercepts the inflow of the metal source, passes purge gas, and remains to the vacuum evaporatio interior of a room is removed after predetermined time. The inflow of purge gas is intercepted after predetermined time, and the metal nitride of a barrier-metal layer is formed on the 1st metal layer which was made to react with the metal source which poured the nitrogen source to the vacuum evaporatio interior of a room, and adsorbed it on said semi-conductor substrate, and was exposed, and a contact hole. Again, the inflow of the nitrogen source is intercepted after predetermined time, purge gas is passed to the vacuum evaporatio interior of a room,



and the nitrogen source which remains to the vacuum evaporatio interior of a room is removed.

[0020] As mentioned above, the barrier-metal layer morphosis is repeatedly executable until it obtains the barrier-metal layer of desired thickness.

[0021] The metal source here  $TiCl_4$ ,  $TiCl_3$ ,  $TiI_4$ , and  $TiBr_2$ ,  $TiF_4$ , 2 (C five H5)  $TiCl_2$ , and 2 (5 (CH3) C5)  $TiCl_2$ , C5 H5  $TiCl_3$ , C9 H10BCl3 N6 Ti, and C9 H7  $TiCl_3$ ,  $TiCl_3$  and  $TiCl_4$  2 (NH3), (C5 5 (CH3)) They are 5 C5 Ti (CH3)3, TDEAT, or TDMAT. (CH3) the nitrogen source -- NH3 \*\*\*\*\* -- making a titanium nitride form by the metal nitride \*\*\*\* -- the metal source -- TaBr5, TaCl5 and TaF5, and TaI5 Or (C5 5 (CH3)) TaCl4 it is -- the nitrogen source -- NH3 \*\* -- it carries out and the TaN film is made to form in a barrier-metal layer

[0022] Moreover, purge gas is Ar or N2. It is desirable to use inert gas.

[0023] The flow rate and inlet time of the metal source poured to the vacuum evaporatio interior of a room, the nitrogen source, and purge gas are taken as the same range as the metal nitride formation approach of this invention mentioned above.

[0024] Moreover, in order to maintain uniformly the pressure of the vacuum evaporatio interior of a room, it is Ar, helium, or N2. The vacuum evaporatio interior of a room can be followed, and a controlled atmosphere can also be passed.

[0025] It is desirable to consider as 400-500 degrees C on the other hand, when using TDEAT and TDMAT as the metal source and using 250-400 degrees C and the metal source the outside of it at the time of formation of a barrier-metal layer.

[0026] Thus, according to constituted this invention, though a level difference spreading property is excellent, the metal nitride which has the low specific resistance below 200micro ohm-cm and low Cl content is obtained. Moreover, an evaporation rate is 20A of outlines, and cycle, forming a CVD-metal nitride at low temperature 500 degrees C or less. A growth rate is 0.25A / cycle. Compared with the metal nitride formation approach by ALE, an evaporation rate is quick.

[0027]

[Embodiment of the Invention] Hereafter, the desirable embodiment of this invention is explained to a detail with reference to an accompanying drawing.

[0028] Drawing 1 is the schematic diagram showing the CVD system for vapor-depositing a metal nitride by the formation approach of this invention.

[0029] Depending on the number of the metal source which makes the number of gas pipes flow in the vacuum evaporatio room 100, and the nitrogen sources, i.e., the number of reaction gases, although two or more gas pipes 114a and 114b are formed in order to make a reaction gas the vacuum evaporatio room 100 flow in the vacuum evaporatio room 100 as illustrated, in the embodiment of this invention, two gas pipes 114a and 114b are formed.

[0030] These two gas pipes 114a and 114b are  $TiCl_4$  as the metal source, when vapor-depositing the TiN film on the semi-conductor substrate 104, although the edge of that one side is respectively connected with the source of supply (not shown) of the metal source, and the source of supply (not shown) of the nitrogen source. It is used and is NH3 as the nitrogen source. It is used. On the other hand, the edge of a side besides gas pipes 114a and 114b is connected with the semi-conductor substrate 104 laid in the vacuum evaporatio room 100, and the shower head 110 from which are separated of more nearly predetermined distance (D of drawing 1 ). therefore, the shower head 110 with which the reaction gas supplied from the source of gas supply (not shown) was connected with the edge of gas pipe 114a and gas pipe 114b -- leading -- the vacuum evaporatio room 100 -- flowing -- the film is formed on the semi-conductor substrate 104 by causing a reaction mutually.

[0031] The shower head 110 has the desirable many-items shower head it is made to flow in the vacuum evaporatio room 100 in the condition that a reaction gas is not mixed, and uses 2 edge shower head in this embodiment. Moreover, in order to supply the purge gas for making the residual gas after a reaction exhaust in the vacuum evaporatio room 100, it is desirable to attach the purge gas supply lines 114c and 114d in gas pipes 114a and 114b.

[0032] A valve 112 is formed in each gas supply Rhine, and purge gas and reactant gas can be made to be able to flow in the vacuum evaporatio room 100 by ON/OFF of a valve 112, or it can intercept. As

for a valve 112, it is desirable to be adjusted by the control section programmed like for example, a pneumatic valve to be able to control ON/OFF of a valve a fixed period beforehand. A reference mark 102 is a heater for heating the semi-conductor substrate 104.

[0033] How to vapor-deposit a metal nitride like TiN by this invention to the semi-conductor substrate hereafter laid in the vacuum evaporatio no interior of a room of the CVD system constituted as mentioned above with reference to drawing 1 and drawing 2 is explained to a detail.

[0034] First, the semi-conductor substrate 104 is inserted in in the vacuum evaporatio no room 100. An individual component [ like a transistor ] whose semi-conductor substrate 104 of this is may already be formed in that front face. (Refer to drawing 1 ) and metal source supply line 114a -- leading -- TiCl<sub>4</sub> The metal source [ like ] is poured ts time in the vacuum evaporatio no room 100. On the other hand, it is Ar and N<sub>2</sub> because of the flow of smooth gas. Conveyance gas [ like ] can be mixed with the metal source, and it can pass in the vacuum evaporatio no room 100. At this time, other valves besides the valve of gas supply Rhine 114a for making the metal source flow are OFF states. Therefore, in the vacuum evaporatio no room 100, it is TiCl<sub>4</sub>. Only the metal source [ like ] is poured. Under the present circumstances, some metal sources which flowed stick to substrate 104 front face chemically and physically, and the remainder remains in the vacuum evaporatio no room 100. Thus, the approach of making only one kind of gas flowing in a fixed time amount vacuum evaporatio no room 100, without making reactant gas flowing into coincidence in the vacuum evaporatio no room 100 is called a gas pulse below (refer to the timing chart of drawing 2 ).

[0035] If the inflow of the metal source is completed in the vacuum evaporatio no room 100, after closing the valve of gas supply Rhine 114a for making the metal source flow, the valve of purge gas supply line 114c is opened, and it is Ar and N<sub>2</sub>. The gas 4 which passes purge gas [ like ] in tp time amount vacuum evaporatio no room 100, and remains in the shower head 110 and the vacuum evaporatio no room 100, for example, TiCl, It is made to exhaust (purge gas pulse phase of drawing 2 ). At this time, the flow rate of purge gas and the pressure of a vacuum evaporatio no room are appropriately adjusted so that the metal source which stuck to the semi-conductor substrate chemically physically is separated and may not be exhausted, and only the source gas which remained to the vacuum evaporatio no interior of a room is made to exhaust.

[0036] And after closing the valve of purge gas supply line 114c, the valve of nitrogen source supply line 114b is opened, and it is NH<sub>3</sub>. TiCl<sub>4</sub> which pours the nitrogen source [ like ] in tr time amount vacuum evaporatio no room 100 and by which it is adsorbed chemically physically on the substrate 104 A metal nitride like TiN is made to form on the semi-conductor substrate 104 by making it react with the metal source [ like ]. Namely, NH<sub>3</sub> TiCl<sub>4</sub> which remains in the vacuum evaporatio no room 100 while passing through a purge gas pulse phase before the nitrogen source [ like ] flows in the vacuum evaporatio no room 100 The metal source [ like ] is beforehand exhausted with a pump (refer to drawing 1 ). Therefore, the nitrogen source like NH<sub>3</sub> is TiCl<sub>4</sub> in the vacuum evaporatio no room 100 except the semi-conductor substrate 104. It does not react with the metal source [ like ]. Therefore, TiCl<sub>4</sub> NH<sub>3</sub> A metal nitride like TiN forms only with the semi-conductor substrate 104 to which it is sticking (NH<sub>3</sub> pulse phase of drawing 2 ).

[0037] Under the present circumstances, it is Ar and N<sub>2</sub> because of the flow of smooth gas. It is conveyance gas [ like ] NH<sub>3</sub> With the nitrogen source [ like ], it can mix and can pass in the vacuum evaporatio no room 100.

[0038] On the other hand, while the metal nitride formation approach by the conventional ALE leaves only the source which is made to purge the source to which it stuck physically and which adsorbed chemically on the substrate, it is fundamentally different from the point of not only the source that adsorbed chemically on the substrate but the source adsorbed physically leaving the metal nitride formation approach of this invention, and making it reacting.

[0039] Next, the nitrogen source for the remainder which the metal source and a reaction are completed and remains in the vacuum evaporatio no room 100 is exhausted, passing through the second same purge gas pulse phase as the purge gas pulse phase where it already explained (purge gas pulse phase of drawing 2 ).

[0040] In order to adjust the pressure in the vacuum evaporatio room 100, while giving said each phase on the other hand Ar and N<sub>2</sub> It is desirable to supply a controlled atmosphere [ like ] continuously in the vacuum evaporatio room 100.

[0041] Thus, the metal nitride formation approach using the gas pulse by this invention is TiCl<sub>4</sub>. Pulse phase -> purge gas pulse phase -> NH<sub>3</sub> Pulse phase -> a metal nitride like TiN of fixed thickness can be vapor-deposited, passing through one cycle which consists of purge gas pulse phases. an evaporation rate -- 20A of outlines, and cycle it is -- since the thickness of a thin film will increase-like proportionally if this cycle is repeated, the thin film of desired thickness can be vapor-deposited to the semi-conductor substrate 104 repeatedly [ of a cycle ]. Under the present circumstances, the flow rate and purge time amount of the flow rate of the metal source which flows in the vacuum evaporatio room 100, the flow rate of the nitrogen source and a gas pulse period, and purge gas can determine the thickness of the metal nitride vapor-deposited to per 1 cycle.

[0042]

[Example] Hereafter, the example which forms the TiN film by this invention is described.

[0043] The TiN film is vapor-deposited by the cycle constituted from under the following reaction conditions by the above-mentioned gas pulse phase on the semi-conductor substrate 104, operating a <example 1> heater (102 of drawing 1 ), and maintaining the temperature of the semi-conductor substrate 104 in low temperature of 500 degrees C or less.

[0044] Vacuum evaporatio condition target matter: TiN controlled atmosphere: The pressure of Ar vacuum evaporatio interior of a room : [ 1 - 20Torr metal source, ] Nitrogen source: TiCl<sub>4</sub> and NH<sub>3</sub>TiCl<sub>4</sub> A flow rate and TiCl<sub>4</sub> Pulse period (ts):1 - 5sccm, 5secNH(s)<sub>3</sub> A flow rate and NH<sub>3</sub> Pulse period (tr):5 - 30sccm, 5sec purge gas, a purge gas flow rate, purge time amount (tp):Ar, 10 - 100sccm, 10sec conveyance gas, a conveyance quantity of gas flow : Ar, time amount [ per 1 cycle 10 - 100sccm ] (tt): -- the condition of the TiN thin film vapor-deposited to the semi-conductor substrate 104 on such conditions 30 sec -- RBS (Rutherford Back Scattering) -- the result checked by law is shown in drawing 3 . The channel of an axis of abscissa shows each channel of MCA (Mutilple Channel Analyzer) by drawing 3 , and it has the relation of the E[eV] =4.05x channel +59.4 with E of energy. Moreover, the axis of ordinate of drawing 3 shows the yield by which the element detected by MCA was standardized.

[0045] The TiN film vapor-deposited and formed in the semi-conductor substrate 104 on the above conditions wears gold peculiar to TiN, and as shown in drawing 3 , it has the perfect presentation of Ti:N=1:1. As shown in drawing 3 , Cl contained in the TiN thin film is below the limit of detection by the RBS method, and is 0.3% or less of the whole element contained in a TiN thin film. Moreover, the specific resistance of the TiN film vapor-deposited and formed in the semi-conductor substrate 104 on the above conditions had the low value the measured value of whose is 130micro ohm-cm extent. On the other hand, according to several experiments, in order to have such an outstanding thin film property, it checked that the thickness of the TiN thin film vapor-deposited per 1 cycle should make 20A or less.

[0046] On the other hand, drawing 4 and drawing 5 are the nitrogen source NH<sub>3</sub> respectively. The result of having measured the specific resistance and the evaporation rate of the TiN film which are vapor-deposited by the approach of this invention is shown changing a flow rate and the vacuum evaporatio room pressure force. An evaporation rate is NH<sub>3</sub> as shown in drawing 4 and drawing 5 . Although it increases by the increment in a flow rate and the vacuum evaporatio room pressure force, thereby, specific resistance also increases. Therefore, it is desirable to consider all of the thickness demanded by application of a metal nitride, an evaporation rate, and specific resistance, and to set up vacuum evaporatio conditions.

[0047] <Example 2> The specific resistance by change of an evaporation rate, the thickness of the TiN film vapor-deposited according to the increment in the number of cycles and an evaporation rate, and vacuum evaporatio temperature was measured per cycle under four vacuum evaporatio conditions as shown in the next table 1. here -- the metal source -- TiCl<sub>4</sub> it is -- in the nitrogen source, NH<sub>3</sub> and purge gas used Ar.

[0048]

[Table 1]

蒸着条件	金属ソースの流量 及び時間	パージガスの流量 及び時間	窒素ソースの流量 及び時間	パージガスの流量 及び時間	圧力	雰囲気ガスの流量
TiN 00	5sccm、 5 秒	40sccm、 5 秒	150sccm、 5 秒	40sccm、 5 秒	3torr	50sccm
TiN 01	3sccm、 3 秒	150sccm、 3 秒	30sccm、 3 秒	150sccm、 3 秒	2torr	30sccm
TiN 02	3sccm、 2 秒	150sccm、 2 秒	50sccm、 2 秒	150sccm、 2 秒	3torr	30sccm
TiN 03	3sccm、 2 秒	150sccm、 2 秒	100sccm、 2 秒	150sccm、 2 秒	3torr	30sccm

[0049] each upper vacuum evaporation condition exception -- per cycle -- an evaporation rate -- an outline -- it was the same as the degree.

[0050] TiN 00:20A / cycle (since 1 cycle is 20 seconds, they are 60A / min)

TiN 01:2A / cycle (since 1 cycle is 12 seconds, they are 10A / min)

TiN 02:3.5A / cycle (since 1 cycle is 8 seconds, they are 26.3A/min)

TiN 03:6A / cycle (since 1 cycle is 8 seconds, they are 45A / min)

Moreover, drawing 6 and drawing 7 are that the thickness and the evaporation rate which are respectively vapor-deposited with the increment in the number of cycles are shown. Vacuum evaporation temperature was made into 500 degrees C only here. An evaporation rate increases slowly ( drawing 7 ) and the thickness vapor-deposited increases in proportion to it, so that a drawing may show and the number of cycles increases ( drawing 6 ). Therefore, the thickness of the TiN film which adjusts and vapor-deposits the number of cycles on certain vacuum evaporation conditions can be adjusted.

[0051] And drawing 8 is a graph which shows the result of having measured the specific resistance of the TiN film which follows vacuum evaporation temperature according to four upper vacuum evaporation conditions. Specific resistance decreases as vacuum evaporation temperature increases from this, especially they are the vacuum evaporation conditions TiN that an evaporation rate is high. It turns out that specific resistance decreases rapidly by 00. Moreover, it turns out that the specific resistance below 200micro ohm-cm is obtained from all four vacuum evaporation conditions at 500 degrees C of outlines.

[0052] Next, the example which applied the metal nitride formation approach of this invention to beer contact is explained to a detail with reference to attached drawing 10 thru/or drawing 21 . Here, in each drawing, the same sign shows the same member.

[0053] First, the 1st metal layer 210 which consists of aluminum is formed on the semi-conductor substrate 200 like drawing 10 , and the TiN film 220 is vapor-deposited as capping film on it. This TiN film 220 can be vapor-deposited by the sputtering approach. Subsequently, if the part which carries out the laminating of the interlayer insulation film 230, and forms beer is etched, it will become like drawing 11 . Before vapor-depositing the TiN film of a barrier-metal layer here, in order to improve the adhesion property of the TiN film, Ti film is formed thinly. This Ti film can also be formed by the sputtering approach.

[0054] Subsequently, if the TiN film of a barrier-metal layer is vapor-deposited by the metal nitride formation approach of this invention mentioned above, it will become like drawing 12 . That is, as the metal source, it is TiCl<sub>4</sub>. Using it, the nitrogen source is NH<sub>3</sub>. It repeats until it uses it, and passes in order of metal source -> purge gas -> nitrogen source -> purge gas and obtains desired thickness within vacuum evaporation equipment like drawing 1 mentioned above. The flow rate of the metal source, the nitrogen source, and purge gas is respectively set to 1 - 5sccm, 5 - 200sccm, and 10 - 200sccm, and each inlet time may be about 1 - 10 seconds. If vacuum evaporation temperature is made into 480 degrees C or less, the vacuum evaporation room pressure force is set to 1 - 20torr and it is required, it is Ar,

helium, or N<sub>2</sub>. A controlled atmosphere, and Ar and N<sub>2</sub> Conveyance gas can be used. Such vacuum evaporation conditions consider vacuum evaporation equipment, an evaporation rate, the thickness of the TiN film vapor-deposited, and specific resistance, and adjust them appropriately.

[0055] Subsequently, the metal plug 250 which consists of a tungsten (W) by the usual approach is formed ( drawing 13 ), and after removing the metal vapor-deposited on the top face of an interlayer insulation film 235 with chemical machinery-polish or etchback ( drawing 14 ), if the 2nd metal layer 260 is formed on it ( drawing 15 ), connection between metal layers will be made.

[0056] On the other hand, although drawing 16 thru/or drawing 21 are the sectional views showing the process which forms support beer contact and it passes through the same process fundamentally with aforementioned drawing 10 thru/or the process of drawing 15 , in order to spread a touch area and to reduce resistance so that drawing 17 may show, the point which forms Support A in the lower part of a contact hole is different. Here, in each drawing, the same sign shows the same member. Like drawing 16 , after Support A forms a contact hole, it is formed by carrying out the wet chemical engraving of the interlayer insulation film 335. Since the process the outside of it is the same as aforementioned drawing 10 thru/or the process of drawing 15 , detailed explanation is omitted.

[0057] Thus, TiFX which the good barrier-metal layer of level difference spreading nature is obtained at low temperature, and is shown in drawing 9 A and drawing 9 B when the metal nitride formation approach by this invention is applied to beer contact AIFX The poor contact [ like ] X can be prevented.

[0058] <Example 3> After vapor-depositing Ti film by sputtering by the thickness of 100A as follows to the contact hole where width of face is different, the TiN film by sputtering which is the TiN film and the conventional approach by the approach of this invention as a barrier-metal layer by which collimation (COL) was carried out was vapor-deposited by the thickness which is different from each other, and the beer resistance at the time of forming a plug by CVD-W was measured. The vacuum evaporation conditions of the TiN film by this invention are only TiN of the vacuum evaporation temperature of 450 degrees C, and the example 2 mentioned above in addition to this. It considered as the vacuum evaporation conditions of 00.

[0059] Beer width of face: 0.24, 0.32, 0.39 micrometers (the depth of beer: 0.9 micrometers)

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**TECHNICAL FIELD**

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[Field of the Invention] This invention relates to the manufacture approach of a semiconductor device, and relates to the metal nitride formation approach by the chemistry gaseous-phase vacuum deposition (it considers as Chemical Vapor Deposition and Following CVD) which uses the metal source and the nitrogen source for a detail as a precursor, and the metal contact formation approach of the semiconductor device using this.

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PRIOR ART

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[Description of the Prior Art] For stabilization of the contact interface of a semiconductor device, the barrier-metal layer which carries out the role which controls the counter diffusion and the chemical reaction between other matter is indispensable. Although a metal nitride like TiN, TaN, and WN is generally widely used as a barrier-metal layer of such a semiconductor device, TiN is the typical matter also in this.

[0003] However, when manufacturing a metal nitride like TiN by the sputtering approach, there is a problem in applying to the semiconductor device which level difference spreading nature is low and integrates highly in order. The cross section at the time of forming the beer contact for connection during metal wiring (via contact) as an example is shown in drawing 9 A and drawing 9 B. Drawing 9 A and drawing 9 B show simple beer contact and support beer contact respectively, and are as follows like the formation fault. After forming the 1st metal layer 30 which consists of aluminum on the semiconductor substrate 20 and forming the TiN film 40 by the sputtering approach as capping film on it, the laminating of the interlayer insulation films 50 and 51 is carried out. subsequently -- the -- one -- a metal -- a layer -- 30 -- a top -- an interlayer insulation film -- etching -- a contact hole -- forming (the process which forms Support A by wet chemical engraving being added in drawing 9 B) -- a glue line -- Ti -- and -- a barrier metal -- a layer -- TiN -- the film -- 60 -- 61 -- having vapor-deposited -- after -- a CVD method -- a contact hole -- filling -- a tungsten -- (-- W --) -- a plug -- 70 -- 71 -- forming . Henceforth, chemical machinery-polish and etchback remove the tungsten for the upper part, and connection between metal wiring is completed by carrying out the laminating of the 2nd metal layer on it (this process was not shown).

[0004] Here, although the conventional approach vapor-deposits the TiN film 60 and 61 of a barrier-metal layer by the sputtering approach which is not good, by the part A which forms the base of a contact hole, dark circles, and support, the thickness of the TiN film becomes thin as the aspect ratio of beer becomes large. Therefore, WF6 Ti or whose aluminum is tungsten source gas by the part where the thickness is thin at the time of tungsten vacuum evaporatio of a consecutiveness process TiFX which it combines with a residual fluorine and is an insulator layer Or AlFX It forms and the poor contact X is invited.

[0005] When increasing vacuum evaporatio time amount and making the thickness of the TiN film 60 and 61 increase as an approach of removing such poor contact, after the thickness of the TiN film increasing, and the upper part of a contact hole becoming narrow or closing only the upper part of a contact hole, possibility that a void will occur at the time of tungsten vacuum evaporatio is high.

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EFFECT OF THE INVENTION

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[Effect of the Invention] As investigated above, according to the metal nitride formation approach by this invention, the metal nitride which has the low specific resistance below 200micro ohm-cm and low Cl content is obtained, excelling in level difference spreading nature. And it is possible to form a metal nitride at low temperature 500 degrees C or less, and an evaporation rate is 20Å of outlines, and cycle. A growth rate is 0.25Å / cycle. Compared with the metal nitride formation approach by ALE, an evaporation rate is far quick.

[0064] Therefore, since the corrosion problem of metal wiring by Cl which remains in the metal nitride as an impurity which is the trouble of the metal nitride vapor-deposited at the conventional elevated temperature 650 degrees C or more, and the problem of high specific resistance are solvable, it is applicable to the beer contact with which an aspect ratio is large with contact and low temperature is demanded, and since the evaporation rate is quick compared with the metal nitride formation approach by ALE, it is suitable for the production process of the semiconductor device as which mass production method is required.

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TECHNICAL PROBLEM

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[Problem(s) to be Solved by the Invention] The purpose is in this invention taking the above demerits into consideration, being thought out, and offering the approach of forming the metal nitride which is satisfied with low temperature of the level difference spreading property of having excelled though the evaporation rate was quick, low high impurity concentration, and low resistivity.

[0011] Other purposes of this invention are to apply the above-mentioned metal nitride formation approach to metal contact of a semiconductor device, and offer the metal contact formation approach of having the barrier-metal layer which is satisfied with low temperature of the level difference spreading property of having excelled though the evaporation rate was quick, low high impurity concentration, and low resistivity.

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MEANS

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[Means for Solving the Problem] The metal nitride formation approach of this invention for attaining the above-mentioned purpose is the metal nitride formation approach by the chemistry gaseous-phase vacuum deposition which uses the metal source (source of a metal), and the nitrogen source (nitrogen source) as a precursor, and is characterized by being made as follows. First, a semi-conductor substrate is inserted in the vacuum evaporatio interior of a room, and the metal source is poured to the vacuum evaporatio interior of a room. The inflow of the metal source is intercepted after predetermined time, and the metal source which flows purge gas into the vacuum evaporatio interior of a room, and remains to the vacuum evaporatio interior of a room is removed. The inflow of purge gas is intercepted after predetermined time, and it is made to react with the metal source which pours the nitrogen source to the vacuum evaporatio interior of a room and by which it was adsorbed on said semi-conductor substrate. Again, the inflow of the nitrogen source is intercepted, purge gas is passed to the vacuum evaporatio interior of a room after predetermined time, the nitrogen source which remains to the vacuum evaporatio interior of a room is removed, and a metal nitride is formed on a semi-conductor substrate.

[0013] The metal nitride formation approach of this invention can repeat the gas inflow cycle passed in order of the above-mentioned metal source -> purge gas -> nitrogen source -> purge gas until it obtains the metal nitride of the thickness of a wish.

[0014] The metal source here  $\text{TiCl}_4$  (titanium chloride),  $\text{TiCl}_3$  (titanium chloride) and  $\text{TiI}_4$  (titanium iodide),  $\text{TiBr}_2$  (titanium bromide) and  $\text{TiF}_4$  (titanium fluoride), 2  $\text{TiCl}_2$  (bis(cyclopentadienyl) titanium dichloride), (C five H5) 2  $\text{TiCl}_2$  (bis(pentamethylcyclopentadienyl) titanium dichloride),  $(\text{CH}_3)_5 \text{C}_5 \text{H}_5 \text{TiCl}_3$  (cyclopentadienyltitanium trichloride),  $\text{C}_9 \text{H}_{10} \text{BCl}_3 \text{N}_6 \text{Ti}$  (hydr-otris(1-pyrazolylborato) trichloro titanium),  $\text{C}_9 \text{H}_7 \text{TiCl}_3$  (indenyltitanium trichloride),  $\text{TiCl}_3$  (pentamethylcyclopentadienyltitanium trichloride),  $(\text{C}_5)_5 (\text{CH}_3)_2 \text{TiCl}_4$  2  $(\text{NH}_3)$  (tetrachlorodiaminotitanium), 5  $\text{C}_5 \text{Ti} (\text{CH}_3)_3$  (trimethylpentamethylcyclopenta dienyltitanium),  $(\text{CH}_3)_3 \text{TiDEAT}$  or  $\text{TDMAT}$  and the nitrogen source can form a titanium nitride by the metal nitride as  $\text{NH}_3$ . The metal source  $\text{TaBr}_5$  (tantalum bromide) and  $\text{TaCl}_5$  (tantalum chloride),  $\text{TaF}_5$  (tantalum fluoride), It is referred to as  $\text{TaI}_5$  or (tantalum iodide)  $(\text{C}_5)_5 (\text{CH}_3)_2 \text{TaCl}_4$  (pentamethylcyclopentadienyltantalum tetrachloride). It is the nitrogen source  $\text{NH}_3$  Carry out, a tantalum nitride is made to form and it gets.

[0015] Moreover, purge gas is Ar or  $\text{N}_2$ . It is desirable to use inert gas.

[0016] As for the flow rate of the metal source which flows into the vacuum evaporatio interior of a room, the nitrogen source, and purge gas, it is desirable to make it respectively like 1 - 5sccm, 5 - 200sccm, and 10 - 200sccm, and, as for the inlet time of each gas, it is desirable to make it about 1 - 10 seconds.

[0017] Moreover, in order to maintain uniformly the pressure of the vacuum evaporatio interior of a room, it is Ar, helium, or  $\text{N}_2$ . A controlled atmosphere can also be continued and passed to the vacuum evaporatio interior of a room.

[0018] It is desirable to make the vacuum evaporatio room pressure force to 0.1 - 10torr, and to make

vacuum evaporation temperature into 250-400 degrees C on the other hand, in forming the TiN film as the metal source using TDEAT or TDMAT. In using the metal source the outside of it, the vacuum evaporation room pressure force is made to 1 - 20torr, and it makes vacuum evaporation temperature into 400-500 degrees C.

[0019] The metal contact formation approach of this invention for attaining other above-mentioned purposes is the metal contact formation approach which forms the 1st metal layer, an interlayer insulation film, a contact hole, a barrier-metal layer, a metal plug, and the 2nd metal layer in order on a semi-conductor substrate, and the process which forms especially a barrier-metal layer is characterized by the following. That is, the metal source is poured and the metal source is made to adsorb to the semi-conductor substrate with which the contact hole which exposes the 1st metal layer to an interlayer insulation film was formed. The metal source which intercepts the inflow of the metal source, passes purge gas, and remains to the vacuum evaporation interior of a room is removed after predetermined time. The inflow of purge gas is intercepted after predetermined time, and the metal nitride of a barrier-metal layer is formed on the 1st metal layer which was made to react with the metal source which poured the nitrogen source to the vacuum evaporation interior of a room, and adsorbed it on said semi-conductor substrate, and was exposed, and a contact hole. Again, the inflow of the nitrogen source is intercepted after predetermined time, purge gas is passed to the vacuum evaporation interior of a room, and the nitrogen source which remains to the vacuum evaporation interior of a room is removed.

[0020] As mentioned above, the barrier-metal layer morphosis is repeatedly executable until it obtains the barrier-metal layer of desired thickness.

[0021] The metal source here  $\text{TiCl}_4$ ,  $\text{TiCl}_3$ ,  $\text{TiI}_4$ , and  $\text{TiBr}_2$ ,  $\text{TiF}_4$ , 2 (C five H5)  $\text{TiCl}_2$ , and 2 (5 (CH3) C5)  $\text{TiCl}_2$ , C5 H5  $\text{TiCl}_3$ , C9 H10BCl3 N6 Ti, and C9 H7  $\text{TiCl}_3$ ,  $\text{TiCl}_3$  and  $\text{TiCl}_4$  2 (NH3), (C5 5 (CH3)) They are 5 C5 Ti (CH3)3, TDEAT, or TDMAT. (CH3) the nitrogen source -- NH3 \*\*\*\*\* -- making a titanium nitride form by the metal nitride \*\*\*\* -- the metal source -- TaBr5, TaCl5 and TaF5, and TaI5 Or (C5 5 (CH3)) TaCl4 it is -- the nitrogen source -- NH3 \*\* -- it carries out and the TaN film is made to form in a barrier-metal layer

[0022] Moreover, purge gas is Ar or N2. It is desirable to use inert gas.

[0023] The flow rate and inlet time of the metal source poured to the vacuum evaporation interior of a room, the nitrogen source, and purge gas are taken as the same range as the metal nitride formation approach of this invention mentioned above.

[0024] Moreover, in order to maintain uniformly the pressure of the vacuum evaporation interior of a room, it is Ar, helium, or N2. The vacuum evaporation interior of a room can be followed, and a controlled atmosphere can also be passed.

[0025] It is desirable to consider as 400-500 degrees C on the other hand, when using TDEAT and TDMAT as the metal source and using 250-400 degrees C and the metal source the outside of it at the time of formation of a barrier-metal layer.

[0026] Thus, according to constituted this invention, though a level difference spreading property is excellent, the metal nitride which has the low specific resistance below 200micro ohm-cm and low Cl content is obtained. Moreover, an evaporation rate is 20A of outlines, and cycle, forming a CVD-metal nitride at low temperature 500 degrees C or less. A growth rate is 0.25A / cycle. Compared with the metal nitride formation approach by ALE, an evaporation rate is quick.

[0027]

[Embodiment of the Invention] Hereafter, the desirable embodiment of this invention is explained to a detail with reference to an accompanying drawing.

[0028] Drawing 1 is the schematic diagram showing the CVD system for vapor-depositing a metal nitride by the formation approach of this invention.

[0029] Depending on the number of the metal source which makes the number of gas pipes flow in the vacuum evaporation room 100, and the nitrogen sources, i.e., the number of reaction gases, although two or more gas pipes 114a and 114b are formed in order to make a reaction gas the vacuum evaporation room 100 flow in the vacuum evaporation room 100 as illustrated, in the embodiment of this invention, two gas pipes 114a and 114b are formed.

[0030] These two gas pipes 114a and 114b are  $\text{TiCl}_4$  as the metal source, when vapor-depositing the TiN film on the semi-conductor substrate 104, although the edge of that one side is respectively connected with the source of supply (not shown) of the metal source, and the source of supply (not shown) of the nitrogen source. It is used and is  $\text{NH}_3$  as the nitrogen source. It is used. On the other hand, the edge of a side besides gas pipes 114a and 114b is connected with the semi-conductor substrate 104 laid in the vacuum evaporation room 100, and the shower head 110 from which are separated of more nearly predetermined distance (D of drawing 1 ).

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## EXAMPLE

[Example] Hereafter, the example which forms the TiN film by this invention is described.

[0043] The TiN film is vapor-deposited by the cycle constituted from under the following reaction conditions by the above-mentioned gas pulse phase on the semi-conductor substrate 104, operating a <example 1> heater (102 of drawing 1), and maintaining the temperature of the semi-conductor substrate 104 in low temperature of 500 degrees C or less.

[0044] Vacuum evaporatio condition target matter: TiN controlled atmosphere: The pressure of Ar vacuum evaporatio interior of a room : [ 1 - 20Torr metal source, ] Nitrogen source: TiCl<sub>4</sub> and NH<sub>3</sub>TiCl<sub>4</sub> A flow rate and TiCl<sub>4</sub> Pulse period (ts): 1 - 5sccm, 5sec NH(s)<sub>3</sub> A flow rate and NH<sub>3</sub> Pulse period (tr): 5 - 30sccm, 5sec purge gas, a purge gas flow rate, purge time amount (tp): Ar, 10 - 100sccm, 10sec conveyance gas, a conveyance quantity of gas flow : Ar, time amount [ per 1 cycle 10 - 100sccm ] (tt): -- the condition of the TiN thin film vapor-deposited to the semi-conductor substrate 104 on such conditions 30 sec -- RBS (Rutherford Back Scattering) -- the result checked by law is shown in drawing 3. The channel of an axis of abscissa shows each channel of MCA (Mutilple Channel Analyzer) by drawing 3, and it has the relation of the E[eV] = 4.05x channel + 59.4 with E of energy. Moreover, the axis of ordinate of drawing 3 shows the yield by which the element detected by MCA was standardized.

[0045] The TiN film vapor-deposited and formed in the semi-conductor substrate 104 on the above conditions wears gold peculiar to TiN, and as shown in drawing 3, it has the perfect presentation of Ti:N=1:1. As shown in drawing 3, Cl contained in the TiN thin film is below the limit of detection by the RBS method, and is 0.3% or less of the whole element contained in a TiN thin film. Moreover, the specific resistance of the TiN film vapor-deposited and formed in the semi-conductor substrate 104 on the above conditions had the low value the measured value of whose is 130micro ohm-cm extent. On the other hand, according to several experiments, in order to have such an outstanding thin film property, it checked that the thickness of the TiN thin film vapor-deposited per 1 cycle should make 20A or less.

[0046] On the other hand, drawing 4 and drawing 5 are the nitrogen source NH<sub>3</sub> respectively. The result of having measured the specific resistance and the evaporation rate of the TiN film which are vapor-deposited by the approach of this invention is shown changing a flow rate and the vacuum evaporatio room pressure force. An evaporation rate is NH<sub>3</sub> as shown in drawing 4 and drawing 5. Although it increases by the increment in a flow rate and the vacuum evaporatio room pressure force, thereby, specific resistance also increases. Therefore, it is desirable to consider all of the thickness demanded by application of a metal nitride, an evaporation rate, and specific resistance, and to set up vacuum evaporatio conditions.

[0047] <Example 2> The specific resistance by change of an evaporation rate, the thickness of the TiN film vapor-deposited according to the increment in the number of cycles and an evaporation rate, and vacuum evaporatio temperature was measured per cycle under four vacuum evaporatio conditions as shown in the next table 1. here -- the metal source -- TiCl<sub>4</sub> it is -- in the nitrogen source, NH<sub>3</sub> and purge gas used Ar.

[0048]

[Table 1]

蒸着条件	金属ソースの流量 及び時間	バージガスの流量 及び時間	窒素ソースの流量 及び時間	バージガスの流量 及び時間	圧力	雰囲気ガスの流量
TiN 00	5sccm、 5 秒	40sccm、 5 秒	150sccm、 5 秒	40sccm、 5 秒	3torr	50sccm
TiN 01	3sccm、 3 秒	150sccm、 3 秒	30sccm、 3 秒	150sccm、 3 秒	2torr	30sccm
TiN 02	3sccm、 2 秒	150sccm、 2 秒	50sccm、 2 秒	150sccm、 2 秒	3torr	30sccm
TiN 03	3sccm、 2 秒	150sccm、 2 秒	100sccm、 2 秒	150sccm、 2 秒	3torr	30sccm

[0049] each upper vacuum evaporatio no condition exception -- per cycle -- an evaporation rate -- an outline -- it was the same as the degree.

[0050] TiN 00:20A / cycle (since 1 cycle is 20 seconds, they are 60A / min)

TiN 01:2A / cycle (since 1 cycle is 12 seconds, they are 10A / min)

TiN 02:3.5A / cycle (since 1 cycle is 8 seconds, they are 26.3A/min)

TiN 03:6A / cycle (since 1 cycle is 8 seconds, they are 45A / min)

Moreover, drawing 6 and drawing 7 are that the thickness and the evaporation rate which are respectively vapor-deposited with the increment in the number of cycles are shown. Vacuum evaporatio no temperature was made into 500 degrees C only here. An evaporation rate increases slowly ( drawing 7 ) and the thickness vapor-deposited increases in proportion to it, so that a drawing may show and the number of cycles increases ( drawing 6 ). Therefore, the thickness of the TiN film which adjusts and vapor-deposits the number of cycles on certain vacuum evaporatio no conditions can be adjusted.

[0051] And drawing 8 is a graph which shows the result of having measured the specific resistance of the TiN film which follows vacuum evaporatio no temperature according to four upper vacuum evaporatio no conditions. Specific resistance decreases as vacuum evaporatio no temperature increases from this, especially they are the vacuum evaporatio no conditions TiN that an evaporation rate is high. It turns out that specific resistance decreases rapidly by 00. Moreover, it turns out that the specific resistance below 200micro ohm-cm is obtained from all four vacuum evaporatio no conditions at 500 degrees C of outlines.

[0052] Next, the example which applied the metal nitride formation approach of this invention to beer contact is explained to a detail with reference to attached drawing 10 thru/or drawing 21 . Here, in each drawing, the same sign shows the same member.

[0053] First, the 1st metal layer 210 which consists of aluminum is formed on the semi-conductor substrate 200 like drawing 10 , and the TiN film 220 is vapor-deposited as capping film on it. This TiN film 220 can be vapor-deposited by the sputtering approach. Subsequently, if the part which carries out the laminating of the interlayer insulation film 230, and forms beer is etched, it will become like drawing 11 . Before vapor-depositing the TiN film of a barrier-metal layer here, in order to improve the adhesion property of the TiN film, Ti film is formed thinly. This Ti film can also be formed by the sputtering approach.

[0054] Subsequently, if the TiN film of a barrier-metal layer is vapor-deposited by the metal nitride formation approach of this invention mentioned above, it will become like drawing 12 . That is, as the metal source, it is TiCl<sub>4</sub>. Using it, the nitrogen source is NH<sub>3</sub>. It repeats until it uses it, and passes in order of metal source -> purge gas -> nitrogen source -> purge gas and obtains desired thickness within vacuum evaporatio no equipment like drawing 1 mentioned above. The flow rate of the metal source, the nitrogen source, and purge gas is respectively set to 1 - 5sccm, 5 - 200sccm, and 10 - 200sccm, and each inlet time may be about 1 - 10 seconds. If vacuum evaporatio no temperature is made into 480 degrees C or less, the vacuum evaporatio no room pressure force is set to 1 - 20torr and it is required, it is Ar,

helium, or N<sub>2</sub>. A controlled atmosphere, and Ar and N<sub>2</sub> Conveyance gas can be used. Such vacuum evaporatio conditions consider vacuum evaporatio equipment, an evaporation rate, the thickness of the TiN film vapor-deposited, and specific resistance, and adjust them appropriately.

[0055] Subsequently, the metal plug 250 which consists of a tungsten (W) by the usual approach is formed ( drawing 13 ), and after removing the metal vapor-deposited on the top face of an interlayer insulation film 235 with chemical machinery-polish or etchback ( drawing 14 ), if the 2nd metal layer 260 is formed on it ( drawing 15 ), connection between metal layers will be made.

[0056] On the other hand, although drawing 16 thru/or drawing 21 are the sectional views showing the process which forms support beer contact and it passes through the same process fundamentally with aforementioned drawing 10 thru/or the process of drawing 15 , in order to spread a touch area and to reduce resistance so that drawing 17 may show, the point which forms Support A in the lower part of a contact hole is different. Here, in each drawing, the same sign shows the same member. Like drawing 16 , after Support A forms a contact hole, it is formed by carrying out the wet chemical engraving of the interlayer insulation film 335. Since the process the outside of it is the same as aforementioned drawing 10 thru/or the process of drawing 15 , detailed explanation is omitted.

[0057] Thus, TiFX which the good barrier-metal layer of level difference spreading nature is obtained at low temperature, and is shown in drawing 9 A and drawing 9 B when the metal nitride formation approach by this invention is applied to beer contact AIFX The poor contact [ like ] X can be prevented.

[0058] <Example 3> After vapor-depositing Ti film by sputtering by the thickness of 100A as follows to the contact hole where width of face is different, the TiN film by sputtering which is the TiN film and the conventional approach by the approach of this invention as a barrier-metal layer by which collimation (COL) was carried out was vapor-deposited by the thickness which is different from each other, and the beer resistance at the time of forming a plug by CVD-W was measured. The vacuum evaporatio conditions of the TiN film by this invention are only TiN of the vacuum evaporatio temperature of 450 degrees C, and the example 2 mentioned above in addition to this. It considered as the vacuum evaporatio conditions of 00.

[0059] Beer width of face: 0.24, 0.32, 0.39 micrometers (the depth of beer: 0.9 micrometers)  
Thickness of the TiN film: 100,200,400,600A (it vapor-deposits by the approach of this invention above), 700A (collimation TiN)

Resistance decreases, so that beer width of face increases on the whole, as shown in a measurement result and drawing 22 , and it turns out that resistance is so small that the thickness of the TiN film by this invention is small. As compared with the collimation TiN film for a comparison, resistance of the TiN film by this invention of 100A thickness appeared similar. Especially when beer width of face was 0.39 micrometers, all of beer resistance of five upper TiN film appeared in resemblance. On the other hand, if it forms on the conditions that an evaporation rate is still slower than this, and specific resistance is small when considering per cycle formation on the vacuum evaporatio conditions that an evaporation rate is quick and specific resistance (20A / cycle) is large (it is 300micro ohm-cm at 450 degrees C) so that the result of an example 2 and drawing 8 may show the TiN film by this invention, it turns out that it can be greatly improved by beer resistance.

[0060] Moreover, it is the graph which shows distribution of beer resistance of each TiN film in case beer width of face is 0.39 micrometers, and, as for drawing 23 , it turns out that the collimation TiN film and all the TiN film by this invention get 1.0 ohms mixed up, and it is equally distributed without a big difference.

[0061] As mentioned above, TiCl<sub>4</sub> And NH<sub>3</sub> Although it explained considering as a precursor and forming the TiN film which is a metal nitride TiCl<sub>4</sub> of the above [ this invention ] not only -- TiCl<sub>3</sub>, TiI<sub>4</sub>, and TiBr<sub>2</sub> -- TiF<sub>4</sub>, 2 (C five H<sub>5</sub>) TiCl<sub>2</sub>, and 2 (5 (CH<sub>3</sub>) C<sub>5</sub>) TiCl<sub>2</sub>, C<sub>5</sub> H<sub>5</sub> TiCl<sub>3</sub>, C<sub>9</sub> H<sub>10</sub>BCl<sub>3</sub> N<sub>6</sub> Ti, and C<sub>9</sub>H<sub>7</sub> TiCl<sub>3</sub>, TiCl<sub>3</sub> and TiCl<sub>4</sub> 2 (NH<sub>3</sub>), (C<sub>5</sub> 5 (CH<sub>3</sub>)) The TiN film which used 5 C<sub>5</sub> Ti (CH<sub>3</sub>)<sub>3</sub>, TDEAT, or TDMAT as a precursor, (CH<sub>3</sub>) And TaBr<sub>5</sub>, TaCl<sub>5</sub>, TaF<sub>5</sub>, and TaI<sub>5</sub> Or (C<sub>5</sub> 5 (CH<sub>3</sub>)) TaCl<sub>4</sub> It can apply to the metal nitride of the TaN film used as a precursor, and most of matter layers further vapor-deposited using the CVD approach.

[0062] It is desirable to make vacuum evaporatio temperature and a pressure into 250-400 degrees C

and 0.1 - 10torr extent unlike the case where other precursors are used, when forming the TiN film, only using TDEAT and TDMAT as a precursor, and since all the precursors for forming the TaN film enumerated upwards are solid-states, when forming source gas, the point which should use the bubbler for solid-states (solid bubbler) is different.

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[Translation done.]



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## DESCRIPTION OF DRAWINGS

### [Brief Description of the Drawings]

[Drawing 1] It is the schematic diagram showing an example of the chemistry gaseous-phase vacuum evaporatio~~no~~ equipment for vapor-depositing a metal nitride on a semi-conductor substrate by this invention.

[Drawing 2] It is the timing chart showing an example of the gas inflow timing for vapor-depositing a metal nitride on a semi-conductor substrate by this invention.

[Drawing 3] It is the graph which shows an example of the RBS result of the metal nitride vapor-deposited by this invention.

[Drawing 4] It is NH<sub>3</sub> when vapor-depositing a metal nitride by this invention. It is the graph which shows the specific resistance of the metal nitride to a flow rate, and an example of the relation of an evaporation rate.

[Drawing 5] When vapor-depositing a metal nitride by this invention, it is the graph which shows the specific resistance of the metal nitride to the vacuum evaporatio~~no~~ room pressure force, and an example of the relation of an evaporation rate.

[Drawing 6] When vapor-depositing a metal nitride by this invention, it is the graph which shows an example of the relation of the vacuum evaporatio~~no~~ thickness of the metal nitride to the number of cycles to repeat.

[Drawing 7] When vapor-depositing a metal nitride by this invention, it is the graph which shows an example of the relation of the evaporation rate of the metal nitride to the number of cycles to repeat.

[Drawing 8] When vapor-depositing a metal nitride by this invention, it is the graph which shows an example of the relation of the specific resistance of the metal nitride to vacuum evaporatio~~no~~ temperature.

[Drawing 9] Drawing 9 A and drawing 9 B are the sectional views showing the beer contact formed by the conventional approach.

[Drawing 10] It is the sectional view showing an example like the beer contact formation fault using the metal nitride formation approach of this invention.

[Drawing 11] It is the sectional view showing an example like the beer contact formation fault using the metal nitride formation approach of this invention.

[Drawing 12] It is the sectional view showing an example like the beer contact formation fault using the metal nitride formation approach of this invention.

[Drawing 13] It is the sectional view showing an example like the beer contact formation fault using the metal nitride formation approach of this invention.

[Drawing 14] It is the sectional view showing an example like the beer contact formation fault using the metal nitride formation approach of this invention.

[Drawing 15] It is the sectional view showing an example like the beer contact formation fault using the metal nitride formation approach of this invention.

[Drawing 16] It is the sectional view showing an example of other examples like the beer contact formation fault using the metal nitride formation approach of this invention.

[Drawing 17] It is the sectional view showing an example of other examples like the beer contact formation fault using the metal nitride formation approach of this invention.

[Drawing 18] It is the sectional view showing an example of other examples like the beer contact formation fault using the metal nitride formation approach of this invention.

[Drawing 19] It is the sectional view showing an example of other examples like the beer contact formation fault using the metal nitride formation approach of this invention.

[Drawing 20] It is the sectional view showing an example of other examples like the beer contact formation fault using the metal nitride formation approach of this invention.

[Drawing 21] It is the sectional view showing an example of other examples like the beer contact formation fault using the metal nitride formation approach of this invention.

[Drawing 22] It is the graph which shows an example of the relation of the beer resistance to the beer width of face at the time of forming a barrier-metal layer by this invention and the conventional approach.

[Drawing 23] It is the graph which shows an example of distribution of the beer resistance at the time of forming a barrier-metal layer by this invention and the conventional approach.

[Description of Notations]

100 -- Vacuum evaporation room

102 -- Heater

104 -- Semi-conductor substrate

110 -- Shower head

112 -- Valve

114 -- Gas pipe

200 -- Semi-conductor substrate

210 -- The 1st metal layer

220 -- TiN film

230 -- Interlayer insulation film

235 -- Interlayer insulation film

240 -- TiN film

250 -- Metal plug

260 -- The 2nd metal layer

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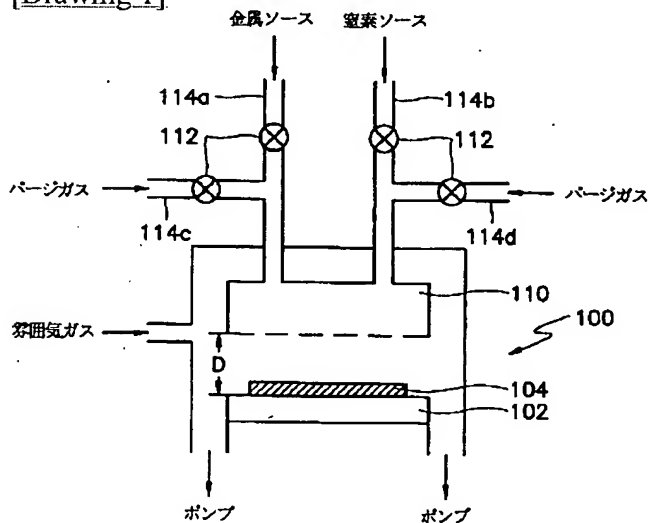
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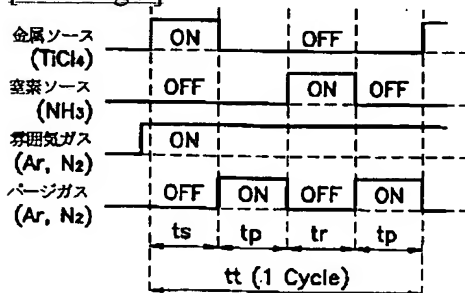
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## DRAWINGS

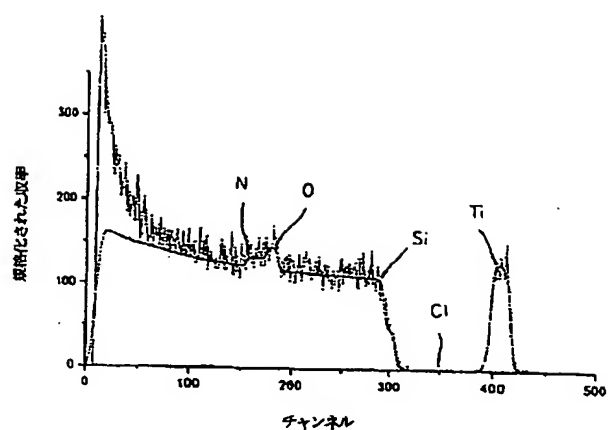
[Drawing 1]



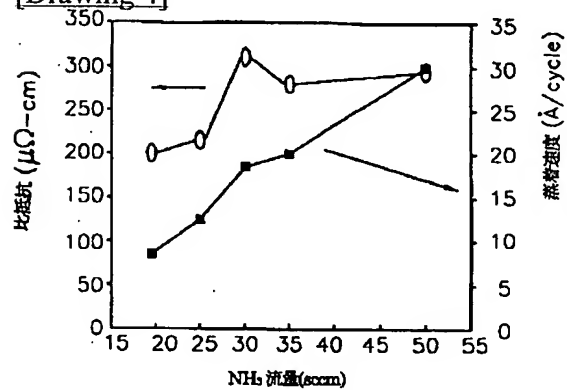
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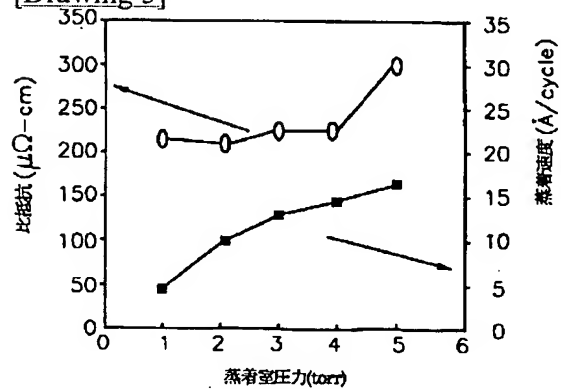
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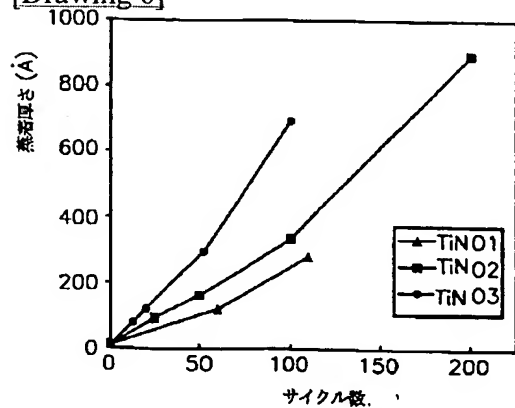
[Drawing 4]



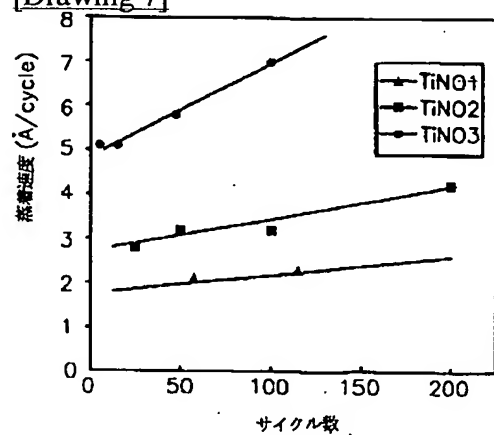
[Drawing 5]



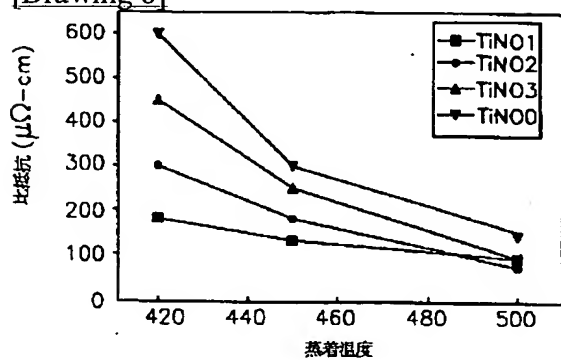
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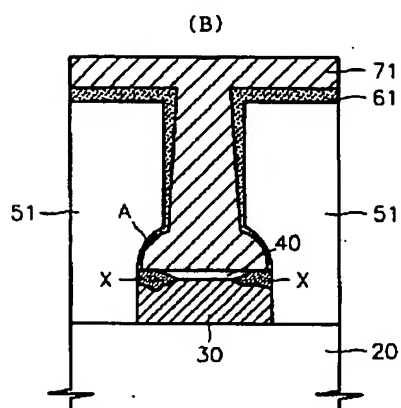
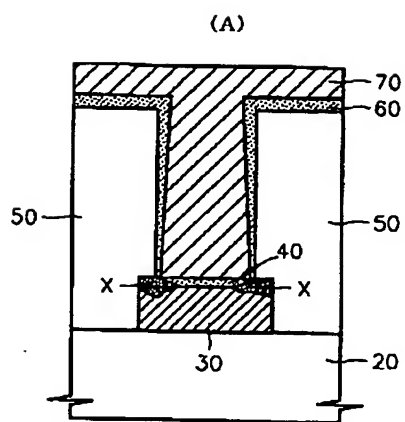
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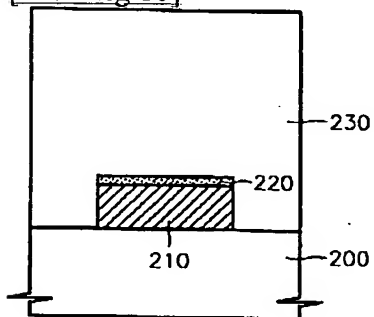
[Drawing 8]



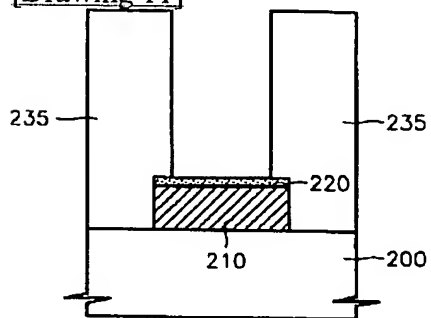
[Drawing 9]



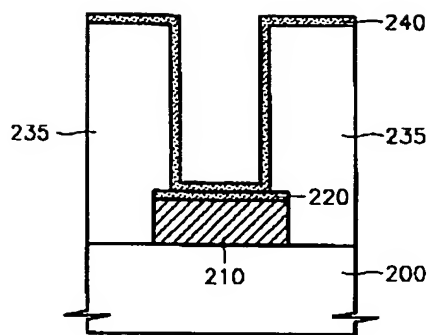
[Drawing 10]



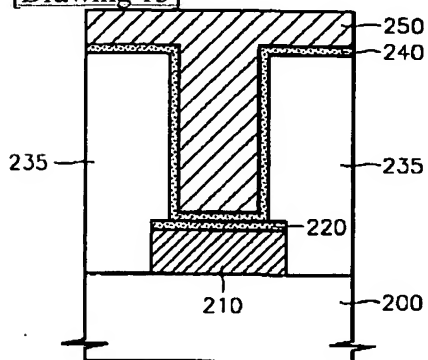
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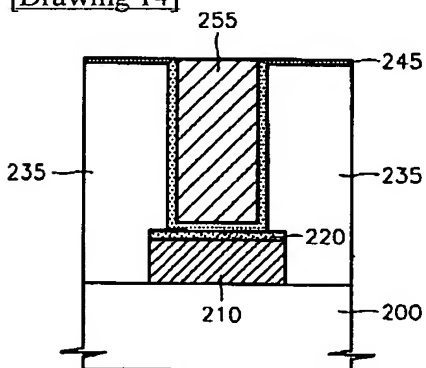
[Drawing 12]



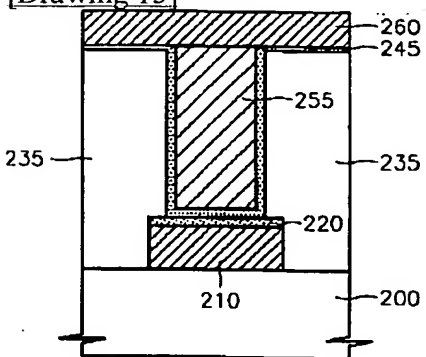
[Drawing 13]



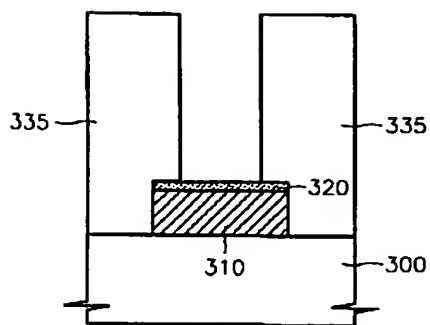
[Drawing 14]



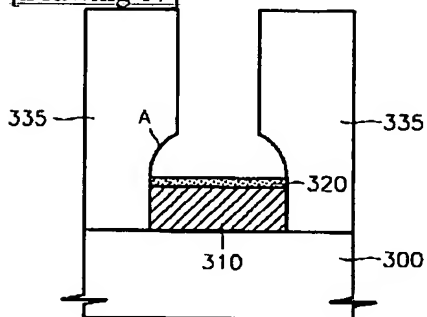
[Drawing 15]



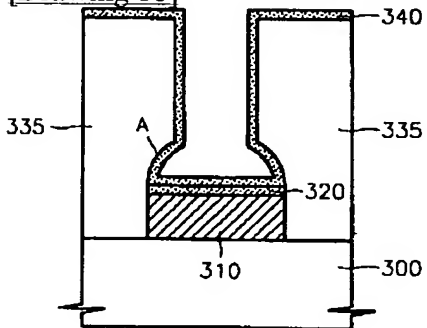
[Drawing 16]



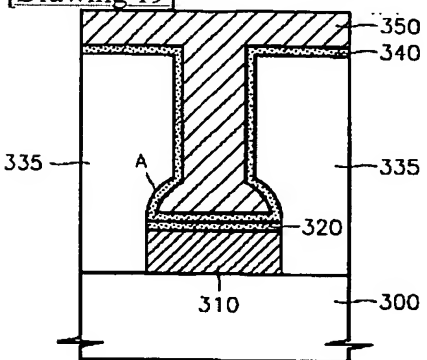
[Drawing 17]



[Drawing 18]

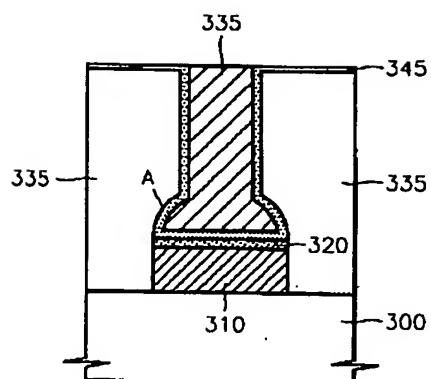


[Drawing 19]

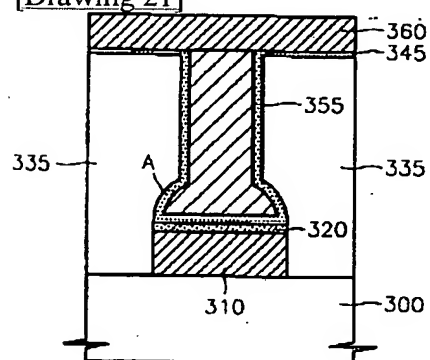


[Drawing 20]

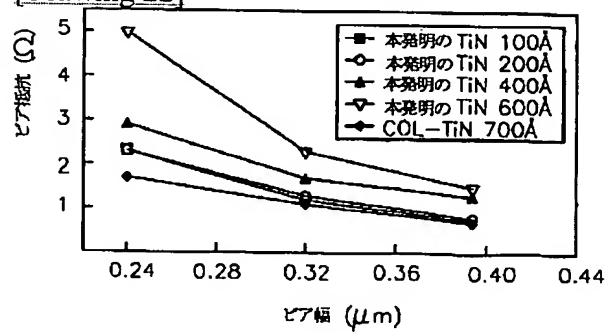




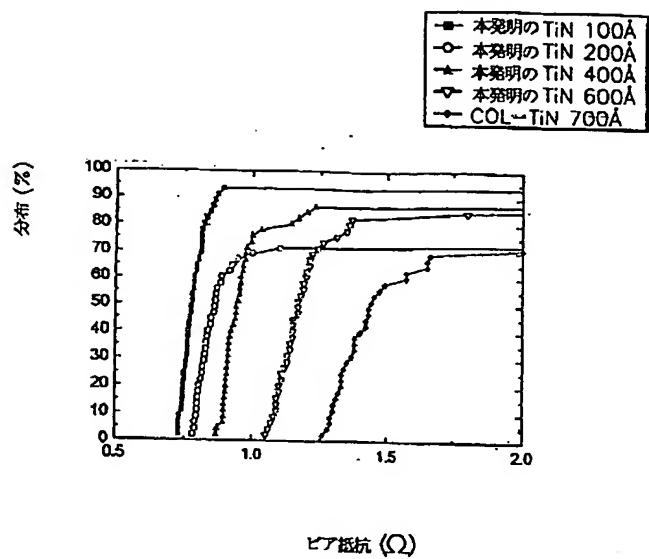
[Drawing 21]



[Drawing 22]



[Drawing 23]



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